Preparation of Supported Nanosized Sulfated Zirconia by Strontia and Assessment of Its Activities in the Esterification of Oleic Acid

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The aim of this study was to examine a new nanocatalyst of SrO/S-ZrO_2 in esterification reaction and the optimum value of strontia loading over the sulfated zirconia. The sulfated zirconia was supported with different molar ratios of strontia in the range of 0.0–0.30, using the solvent-free method. The samples were characterized using XRD, FT-IR, BET and TEM analysis and their activity were investigated in esterification reaction of oleic acid. The findings of this study revealed that 25 mol % SrO/S-ZrO_2 had the highest yield in the esterification reaction. It was also concluded that strontia-supported sulfated zirconia could improve the low reusability of the catalyst. Furthermore, 95 % conversion was also obtained at optimized conditions (i.e., 100 °C, 2 wt. % of catalyst, 6:1 molar ratio of methanol/oleic acid and for a period of 30 minutes).

Key words:
esterification, sulfated zirconia, strontia, solvent-free method

Introduction

In recent years, governmental health agencies are highly concerned about the toxic emissions from diesel engines. Among fuel alternatives, biodiesel has the highest potential. Biodiesel has similar properties as diesel and could be directly utilized for diesel engines. The main advantages of biodiesel are that it could be used without modification, it is renewable, non-toxic, environment-friendly, and generates less harmful emissions such as sulfur oxide, aromatics and CO.[1] Biodiesel is generally produced from transesterification of fats and vegetable oils with a short-chain alcohol in the presence of a catalyst.[2] Recently, non-edible oil as a feedstock (e.g., Jatropha, algae and waste cooking oil) was of prime concern for the reduction of biodiesel production costs.[3] However, these feedstocks have a high percentage of free fatty acids (FFA) that could not be converted to biodiesel with homogeneous catalysts due to the production of soap as a by-product from the reaction of FFA and homogeneous catalyst. It must be noted that biodiesel purification and separation produces huge amounts of wastewater. Therefore, the heterogeneous catalysts have been utilized for the conversion of FFAs to biodiesel.[4,5]

Amongst different heterogeneous catalysts, sulfated zirconia exhibits a high ability of carrying out both esterification and transesterification reaction.[6,7] Furthermore, sulfated zirconia has a towering catalytic activity of isomerizing alkanes at relatively low temperature.[8] However, its main drawbacks are its deactivation after one reaction, and the ability to be easily regenerated by simple re-calcinations in air.[9] Therefore, many researchers have attempted to improve the properties of the catalyst by supporting it with another metal oxide. In previous works conducted by the authors, it was reported that sulfated zirconia modified with strontia (SrO/S-ZrO_2) and alumina by free solvent method has higher catalytic activity than pure sulfated zirconia.[10,11] The authors also demonstrated that there is a good agreement between their findings and those conducted by Yee *et al.*[12] Nonetheless, more work is needed to evaluate the properties of the catalyst, such as optimum amount of support loading and reusability of the catalyst.

Therefore, the aim of this study was to optimize strontia loading percentage on sulfated zirconia and enhance its reusability. To obtain these objectives, the catalysts were characterized by XRD, BET, FT-IR and TEM. Acidity and catalytic activity were also examined by NaOH titration and esterification of oleic acid, respectively. Furthermore, the influence of different parameters for the best conversion percentage of the oleic acid as FFA to its methyl ester has also been examined.

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Experimental procedure

Materials

In this work, $ZrOCl_2 \cdot 8H_2O$ and $SrSO_4$ with 98 % purity was utilized. Furthermore, $(NH_4)_2SO_4$, oleic acid, methanol, ethanol, sodium, and calcium hydroxide with higher purity were also prepared from the Merck Company.

Catalyst synthesis

Pure sulfated zirconia was prepared by the solvent-free method.[11] The sulfated zirconia modified with strontia was prepared by the solvent-free method as described below:

1 mol of $ZrOCl_2 \cdot 8H_2O$ with 6 mol of $(NH_4)_2SO_4$ and $SrSO_4$ with molar ratio ranging from 0.0 to 0.30 (0.0 – 0.17 wt. %) were ground in ceramic mortar for 20 minutes at room temperature. After standing at room temperature for 18 hours, it was calcined for 5 hours at 500 °C.

Catalyst characterization

Phase identification and crystallite size of the samples were assessed by X-ray diffraction from UNISANTIS/XMP 300, using Cu K_α radiation (λ = 0.15406 nm) at 45 kV and 80 mA over a 2θ ranging from 20°–70° at a scanning speed of 10° min^{-1}. The crystalline size of tetragonal and monoclinic phases was computed from Scherrer's equation as follows:[13]

$$D = K\lambda/\beta \cos\theta \qquad [1]$$

where K = 0.9, D represents the crystallite size, λ is the wavelength of Cu K_α radiation, and θ designates the corrected half-width of the diffraction peak angle.

In this study, surface area, pore volume and average pore size of the synthesis catalysts were measured by BET method using an AUTOSORB 1 of QUANTACHROME U.S.A. Furthermore, the spectrums of samples were recorded using Fourier transform infrared spectroscopy (FT-IR) on a SHIMADZU 4300 spectrometer in the range of 400–4000 cm^{-1}. A standard KBr technique was also employed for the samples preparation. In order to determine the catalyst acidity defined as mmol of NaOH per gram of catalyst, 0.2 g of the catalyst was dissolved in 10 mL^{-1} of deionized water and was titrated by aqueous solution of 0.1 mol L^{-1} NaOH. In this work, acidity was defined as mmol of NaOH per gram of catalyst. The method is based on the aqueous ion-exchange of the catalyst H^+ ions with Na^+ ions.[14]

To estimate the best nanocatalyst particle size, a LEO 912AB *transmission electron microscopy* (TEM) was employed and compared with the pure sulfated zirconia.

Catalysts testing

To assess the catalytic activity, the esterification reaction was carried out in a stainless steel reactor that was placed in a glycerol bath as it was required to control the temperature. The reaction was carried out at 90 °C for 30 minutes, utilizing 10 g of oleic acid, 9 molar ratio of methanol/oleic acid, and 0.3 g of catalyst. After esterification reaction, the catalysts and water were simply separated from the product mixtures by filtration and decanter, respectively. Excess methanol was then removed by heating to 80 °C. The conversion of oleic acid into its ester (the catalytic activity) was calculated based on the reduction of the acidity index of the products as compared with the acidity index for the initial oleic acid.[15]

Results and discussions

Assessment of the amount of strontia loading on sulfated zirconia

The plots of XRD analysis for the supported sulfated zirconia with different percentages of strontia are shown in Fig. 1. Fig. 1a describes the behavior of pure sulfated zirconia at 500 °C. It reveals that, for the pure sulfated zirconia, only a small peak of monoclinic phases was observed at 2θ = 28.2°. Moreover, the tetragonal phases of zirconia was also observed at 2θ = 30.2°, 35.4° and 50.2°. It was also observed that a small amount of strontia loading over sulfated zirconia would cause a significant change in the structure of catalyst peaks. For 15 % SrO/S-ZrO_2, a new monoclinic and tetragonal phase of zirconia also forms at 2θ = 31.5°, 33.5°, 49.5° and 34.5°, 60°.[16,17]

The presence of strontium groups and their perching between zirconia crystalline and absorbance of sulfate ions would reduce aggregation of sulfate ions on zirconium crystals. This could be caused by the phase transformation from tetragonal to monoclinic.[14] Enhancement of strontia entirely annihilates the balance between zirconia crystal and sulfate ions. Therefore, the tetragonal phases transform to monoclinic phases, hence causing a reduction in activity. Fig. 1 also demonstrates that further addition of strontium sulfate loading would cause the enhancement of sulfate ions on zirconia crystals. It has been shown that zirconia crystalline in 25 mol. % SrO/S-ZrO_2 (Fig. 1d) bonds more freely with sulfate ions owing to the formation of the new structure of $SrZrO_3$. Further enhancement of loading up to 30 mol. %, would also cause some tetragonal or monoclinic phases to transform into a new structure of $SrZrO_3$, in particular at 2θ = 35.4°, 60° and 63.1°.[18]

As shown in Table 1, a reduction in the fraction of tetragonal phases would be observed with the en-

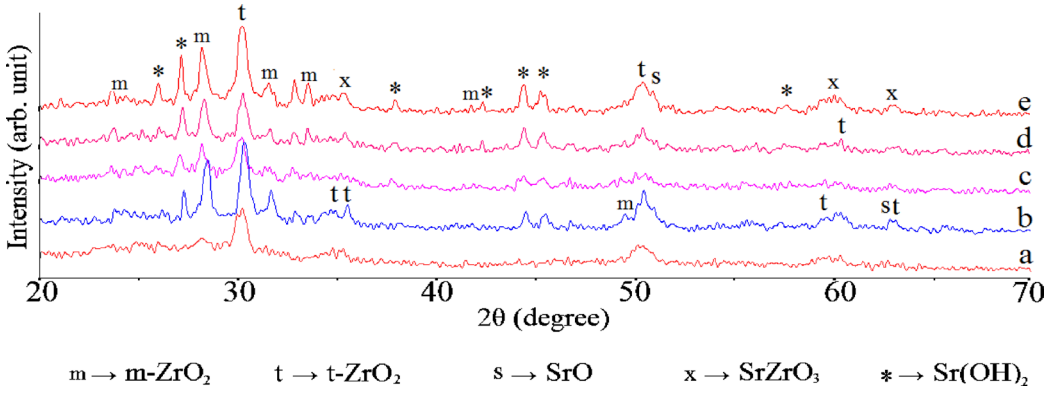

Fig. 1 – *XRD plots of sulfated zirconia supported with a) 0 b) 15 c) 20 d) 25 e) 30 mol. % of strontia*

Table 1 – *Properties of strontia-supported sulfated zirconia*

Catalyst	Strontia loading (%)	Tetragonal phases (%)	Crystalline size (nm)			Conversion (%)
			tetragonal average	monoclinic average	all crystals average	
S-ZrO_2	0	68.2	14.3	13.1	13.7	88.36
SrO/S-ZrO_2	15	62.1	10.2	14.8	13	88.94
SrO/S-ZrO_2	20	80	9.8	13.2	12.4	91.13
SrO/S-ZrO_2	25	82.2	9.0	12.1	9.4	94.88
SrO/S-ZrO_2	30	34.4	12.4	13.8	16.3	25.45

hancement of SrO on the S-ZrO_2. Ramu *et al.* also reported that the catalytic activity has a direct relationship with the fraction of tetragonal phases.[19] Furthermore, the catalytic activity increases with the enhancement of strontium sulfate loading. Nevertheless, the fraction of tetragonal phases and activity of the catalyst reduces with enhancement of further strontia loading up to 25 mol. %.

Table 2 demonstrates the BET surface area measurements for the catalysts. It reveals that strontia loading decreases the BET surface area sharply, which is in good agreement with studies conducted by other researchers.[20] It was concluded that strontia crystals assemble on surface or in pores of sulfated zirconia.

Table 2 – *BET surface area analysis*

Catalyst	Strontia loading (%)	Surface area (m^2 g^{-1})	Pore diameter (nm)	Pore volume (cm^3 g^{-1})
S-ZrO_2	0	120.6	14.2	0.34
SrO/S-ZrO_2	15	6.14	8.3	0.0127
SrO/S-ZrO_2	20	3.95	7.8	0.0075
SrO/S-ZrO_2	25	1.8	7.6	0.0034
SrO/S-ZrO_2	30	0.9	10.1	0.0019

Fig. 2 demonstrates the FT-IR spectrum of absorption bands of sulfated zirconia supported by strontia. As shown in Fig. 2, the bands at 1100, 1140 and 1380 cm^{-1} exhibit a stretching vibration of sulfate ions, which corresponds to zirconium cation.[21] A stretching vibration peak corresponding to S=O was observed at 1223 cm^{-1}. Furthermore, stretching vibration bands of Zr-O were also observed at 420, 445, 630 and 750 cm^{-1} where the peak at 1020 cm^{-1} corresponds to stretching vibration bands of Zr=O.[7] The peaks of sulfate ions at 1380 cm^{-1} and 1223 cm^{-1} correspond to the zirconium cation and oxygen anion, respectively, and they would disappear with the enhancement of loading. It is also worth noting that a new peak of monoclin-

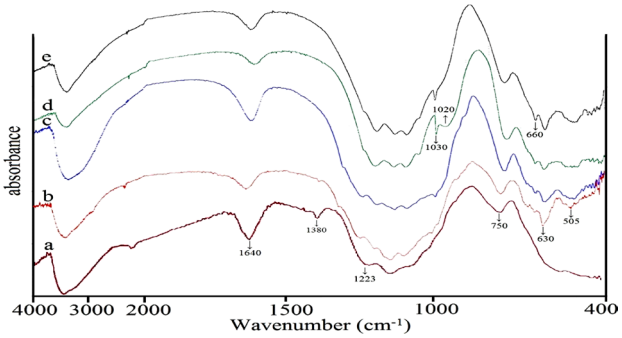

Fig. 2 – *FT-IR spectrum of sulfated zirconia supported with a) 0 b) 15 c) 20 d) 25 e) 30 mol. % of strontia*

ic phases of zirconia was also observed at 505, 520 and 580 cm^{-1} that corresponds to the conversion of some tetragonal to monoclinic. In addition, peak at 660 cm^{-1} was also observed, which corresponds to bands between strontia and zirconia.[22] A band at 1640 cm^{-1} and 3445 cm^{-1} was also observed, which corresponds to the bending and stretching mode of O─H, respectively.[23]

Table 3 exhibits the acidities of the samples studied in this work. It is known that acidity plays an important role in the catalytic activity for the conversion of free fatty acid (FFA) to biodiesel.[19]Wan Omar and co-workers also reported that loading of strontia onto zirconia would cause the enhancement of the basicity.[24] Therefore, the amphoteric property of the zirconia increases with strontia and sulfate ions, and the activity of catalyst rises significantly.

Table 3 – *Acidities of the samples*

Catalyst	Strontia loading (%)	Acidity (mmol NaOH g^{-1} cat.)
$S\text{-}ZrO_2$	0	4.5
$SrO/S\text{-}ZrO_2$	15	4.6
$SrO/S\text{-}ZrO_2$	20	6.0
$SrO/S\text{-}ZrO_2$	25	6.8
$SrO/S\text{-}ZrO_2$	30	2.8

Therefore, the main advantage of sulfated zirconia modified with 25 % strontia is that it possesses all the active crystals, such as zirconia (monoclinic and tetragonal), strontia, SO_4^{2-} and $SrZrO_3$, and causes both to own powerful acidic and basic sites. Therefore, it could be utilized as a catalyst for both esterification and transesterification reactions.

Fig. 3 exhibits the TEM images of 25 mol. % $SrO/S\text{-}ZrO_2$ which are considered the best catalysts for the esterification reaction. It demonstrates that the particle size of zirconia crystals reduces to about 6 nm; thus, enhancing the catalytic activity.

Optimization of esterification reaction of oleic acid with 25 mol. % $SrO/S\text{-}ZrO_2$

Fig. 4 exhibits the effect of reaction temperature on the esterification reaction of oleic acid. It demonstrates that the conversion increases sharply with enhancement of temperature. It is worth noting that a temperature increase would enhance the reaction rate; therefore, early achievement of equilibrium point was obtained.[25] Fig. 4 also demonstrates that the yield increases with enhancement of temperature up to 100 °C; however, no significant changes in the yield were observed after this point. Therefore, 100 °C could be chosen as an optimum

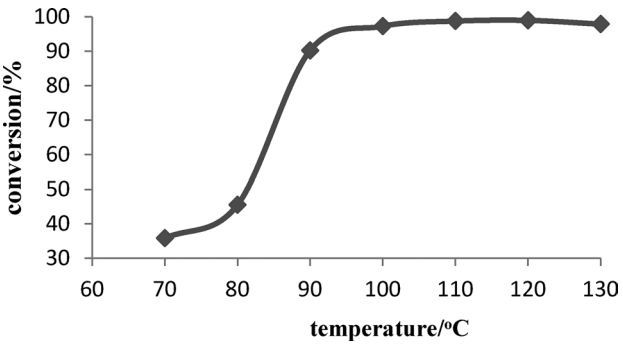

Fig. 4 – *Influence of reaction temperature on conversion of oleic acid. Reaction condition: Methanol/Oleic acid: 9/1, amount of catalyst: 3 wt. %, duration: 30 min.*

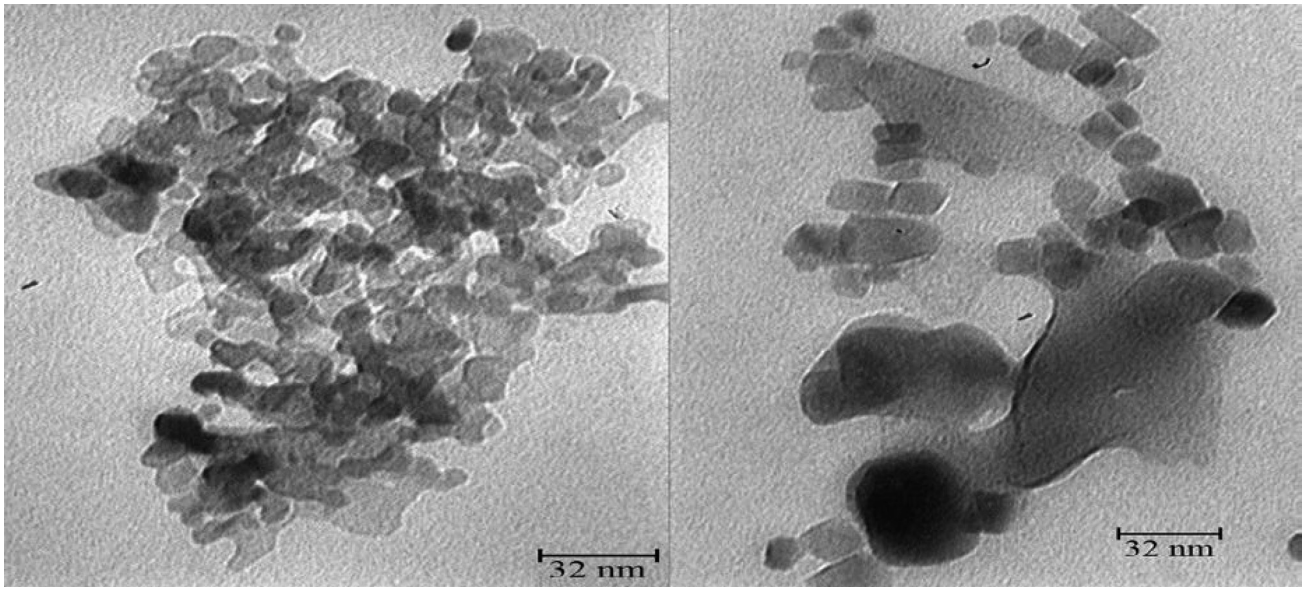

Fig. 3 – *TEM images: right) $S\text{-}ZrO_2$ left) 25 mol. % $SrO/S\text{-}ZrO_2$*

reaction temperature, considering the energy consumption cost and the stability conditions of the experimental set-ups.

The effect of the catalyst amount on the yield of fatty acid methyl ester (FAME) is shown in Fig. 5. The yield increases sharply with enhancement of the catalyst up to 2 %. It was reported that specified active sites of catalysts are required for the conversion of FFA to FAME and more catalyst consumption has no significant effect on the yield.[26] Therefore, the optimum amount of the catalyst was chosen to be 2 wt. %.

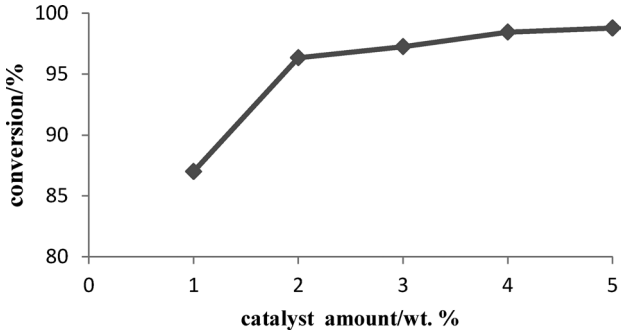

Fig. 5 – *Effect of catalyst weight percentage on the conversion of oleic acid. Reaction condition: T: 100 ˚C, Methanol/Oleic acid: 9/1 mol. %, duration: 30 minutes.*

The effect of the molar ratio of methanol/oleic acid on the yield at a temperature of 100 °C, 2 wt. % of catalyst and for a period of 30 minutes is shown in Fig. 6. It reveals that the conversion enhances as the methanol mole percentage increases accordingly, and maximum yield was achieved at ratio of 12:1. Since esterification reaction is reversible, enhancing the amount of reactants would drive the reversible reaction into forward direction. thus, it was advantageous to utilize a larger amount of methanol. However, percentage of yield would decrease with the further addition of methanol up to the ratio of 12:1.[27] However; no increase in the yield was observed when the methanol ratio exceeded 6:1. Therefore, in this work, a methanol ratio of 6:1 has been chosen in order to lower the cost and increase the methanol recovery.

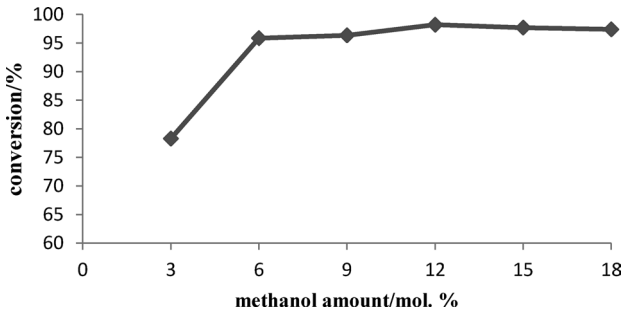

Fig. 6 – *Effect of methanol on the conversion of oleic acid. Reaction condition: T: 100 ˚C, catalyst weight percentage: 2 %, duration: 30 min.*

The reaction time was also investigated for the optimum conditions of esterification reaction at 100 °C, 2 wt. % of catalyst, and molar ratio of 6:1 for methanol/oleic acid. As shown in Fig. 7, the yield increases sharply with the reaction for the first 20 minutes; however, it decreases over the next 40 minutes due to reverse action of the reaction. However, the changes in yield ranging from 30 to 40 minutes were not significant. Thus, duration of 30 minutes was adequate to complete the reaction.

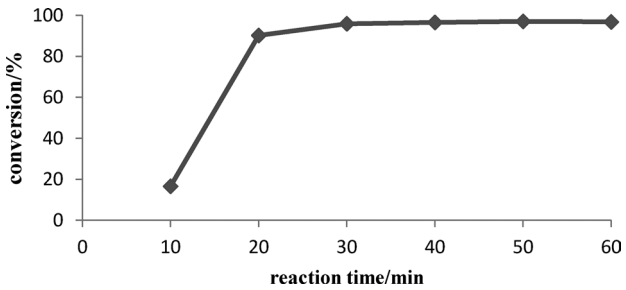

Fig. 7 – *Effect of reaction time on the conversion of oleic acid. Reaction condition: T: 100 ˚C, catalyst weight percentage: 2 %, Methanol/Oleic acid: 6/1 mol. %.*

A comparative study has been conducted between the findings of the present study for the optimum conditions with those reported by Mongkolbovornkij *et. al* (93 % at 90 °C, 9 molar ratio, 1 wt. % and 2 h),[4] Hu *et. al* (122 °C, 2 mol ratio of the fatty acid to 1-butyl alcohol, 1 g/0.1 mol of catalyst to the fatty acid and reaction time of 2 h),[9] Lopez *et. al* (65 % at 75 °C, 3 wt. % of sulfated zirconia, 7 molar ratio of ethanol/caprylic acid and 4 h)[29] and other researchers.[6,14,28] From the findings of this study, it was concluded that the above named catalyst has a high capacity for converting FFA to biodiesel.

Reusability

The main setback in utilizing sulfated zirconia is its low reusability.[4] However, Liu *et al.* reported that SrO could be utilized as much as ten times without reduction in the yield.[30] In order to assess the reusability of 25 mol. % SrO/S-ZrO_2, the catalyst was washed three times with methanol after the esterification reaction, then heated to 120 °C, and finally calcined at 500 °C for 1 hour. As Fig. 8 demonstrates, strontia could significantly enhance the reusability of the catalyst. The findings of this work reveal that the yield for conversion of oleic acid to biodiesel at second to third and fourth times decreases to about 89.96, 85 and 80.81 percent, respectively. Furthermore, the catalytic activity drops sharply at the fifth time as much as 65.25 %. It is

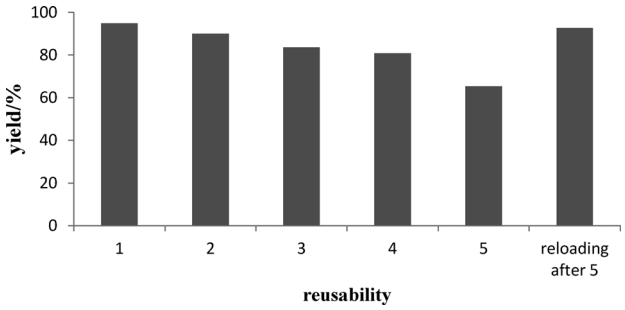

Fig. 8 – *Reusability of catalyst in esterification reaction. Reaction condition: T: 100 ˚C, catalyst weight percentage: 2 %, Methanol/Oleic acid: 6:1 mol. %, duration: 30 minutes.*

due to a reduction in sulfate ions by dissolution in product mixture and deforming of catalyst structure. The yield enormously enhances when the five-time reacted catalyst is ground with an ammonium sulfate (weight ratio 1/3 of catalyst weight) in a mortar after washing, and calcined under similar above conditions. Therefore, the properties of catalyst could be recovered simply by loading ammonium sulfate onto the reacted catalyst. Moreover, strontia could truly improve the drawback of sulfated zirconia reusability.

Conclusion

In this work, properties of the prepared sulfated zirconia supported by strontia using free solvent method were investigated. Enhancement of catalyst activity was observed after loading 25 mol. % of strontium sulfate onto sulfated zirconia. An increase in the percentage of tetragonal phase and acidity decreased the particle size accordingly. The findings of this work also revealed that the reusability of sulfated zirconia could be enhanced by supporting the zirconia with strontia by a factor of four. It was also concluded that the strontia loading would also improve the esterification reaction conditions significantly. In addition, the findings of the present study suggest that 96 percent of oleic acid could be converted to its methyl ester under the following operating conditions: temperature of 100 °C, 2 wt. % of catalyst, 6:1 molar ratio of methanol/oleic acid, and duration of 30 minutes.

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